Nanomaterials: Opportunities and Challenges for Aerospace

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Nanomaterials are regarded world-wide as key materials of the 21st Century. Also in aerospace a high potential for nanomaterials applications is postulated and technological breakthroughs are expected in this area. In this context, improvements based on these materials are to be considered both in a short to medium-term time scale as well as on a long-term basis in view of different prospective studies.

Some applications are feasible in a short to medium-term time horizon like:

a) lightweight and mechanically outstanding structures based on nano-composites, specially for harsh environments, high temperatures,…
b) improved and smaller systems and controls based on microsensors, on smart nanomaterials and/or on embedded actuators for on-line monitoring, self-calibration, self-regulation, or self-healing applications
c) Thermal and mechanical protection layers with outstanding tribological characteristics for engine or landing gear parts made of nanostructured materials
d) Filtration, cleaning and absorption of non-wanted specimen obtained from aerogels

The long-term applications are based on strategic actuations like imitating nature or on molecular nanotechnologies, where material synthesis “a la carte” can be expected.

Anyhow, all these opportunities will become real products if all the challenges that these new technologies imply can be overcome:

a) Technical challenges
b) Regulations and standards
c) Cost and quantities

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1. INTRODUCTION

Nanotechnologies are regarded world-wide as key technologies of the 21st Century. Nano products and processes hold an enormous economic potential for the markets of the future. The production of ever smaller, faster and more efficient products with acceptable price-to-performance ratio has become an increasingly important success factor in the international competition of many sectors. Also in aerospace a high potential for nanotechnological applications is postulated. These technologies could contribute significantly to solutions and technological breakthroughs in this area. In this context, improvements based on these technologies are to be considered both in a short to medium-term time scale as well as on a long-term basis in view of visionary applications.
Some of the challenges for the space are related to, reliability, safety or weight of the structures. Revolutionary solutions can be found within advanced nanomaterials like nanoporous membranes, self-healing nanomaterials, high strength nanocomposites or adaptive and actuating nanostructures. Anyhow, all these opportunities will be possible if all the challenges that these new technologies imply can be overcome:

a) Technical challenges: the manipulation and observation of the materials and systems of micro and nanoscopic size is not obvious. Reliability, reproducibility, etc… need to be addressed to obtain real products
b) Regulations and standards: are another important aspect in these new technologies, as many concerns are arising in terms of toxicological impact as well as in the standardization of the specifications
c) Cost and quantities: can be another issue while these materials are under development as no major manufacturer is willing to produce big quantities, price can not lower to acceptable numbers

Once those challenges are addressed the impact of nanotechnologies will be enormous, specially in technology-demanding sectors as Space. Lighter and stronger materials lead to: longer range missiles, greater payload for launch vehicles, lower cost to orbit. Smart or adaptive materials lead to sel-repairing, actuating or multifunction mechanisms.

2. NANOMATERIALS

Nanomaterials have generated tremendous interest because they present an opportunity to deliver unprecedented material performance. This opportunity is based on the unique properties (mechanical, electronic, thermal, magnetic,..) that vary abruptly with changes in the size of the material at the nanoscale (1-100nm). This step-like changes in nanoscale properties suggest both enormous potential and challenges.

To date, understanding of nanoscale materials and their properties has been achieved primarily through empirical or discovery-based research. A full understanding and development of nanomaterials will be accelerated by a systematic and interdisciplinary approach to fundamental physics, chemistry

and materials science. Working at the nanoscale offers the opportunity to fully exploit design and create materials with functions and properties needed to solve specific problems. The solution-oriented approach will increase the efficiency of materials development and should accelerate the commercial introduction of beneficial products. In addition, the commercialisation of nanomaterials will require the establishment and consolidation of specifications, manufacturing standards as well as the focused applications.

Once the design of the material is well understood, the handling of materials at atomic or molecular size is the next challenge to obtain the desired properties of the material and final products. Bottom-up approaches or top-down miniaturization are both candidate nanotechnologies and should be chosen depending on the final application. Self-assembly or AFM based mechanical handling are bottom-up technologies being developed to conform the final structures but with a lot of industrial drawbacks as the throughput is really low and the maximum sizes obtained are in the range of 10nm. Top-down technologies are based on microtechnologies and microelectronic field technologies, basically lithography and similar ways of structuring in nano or micro geometries or patterns. Dimensions lower than 40nm have not been feasible up to now by these technologies.

Opportunities presented by nanomaterials have been widely documented and examples of commercial successes appear in the media. Aerospace is a yet not expanded sector but with great potential based on their demand of technical and specific materials. Real problems and applications can be addressed with this new perspective on the design of novel materials that could revolutionize the sector.

3. NANOSTRUCTURED COATINGS

Coating processes have many applications in the aerospace industry: to improve durability, reliability and performance of various components; to resist erosion, sliding and fretting wear or to improve surface quality; and to produce corrosion resistant coatings for combating pitting, exfoliation, oxidation or hot corrosion; or as thermal barriers for vehicles or landing gears applications.

Currently under development, there are multifunctional nanocoatings for aerospace that can provide corrosion protection using environmentally safe materials; sense corrosion and mechanical damage of aircraft skin; initiate responses to sensed damage either as alarm changes in colour or real self-healing behaviours; and improve fatigue resistance.

Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique physical-chemical properties [1,2,3]. There are many types of design models for nanostructured

[1] J. Musil, Surf.Coat. Technolo. 125 (2000) 322
[2] P. Holubar, M. Jilek, M. Sima, surf. Coat. Technol. 133-134 (2000) 145
[3] S. Veprek, S. Reiprich, Thin Solid Films 268 (1995) 64

coatings, such as nanocomposite coatings, nano-scale multilayer coating, superlattice coating, nano-graded coatings, etc. A nanocomposite coating comprises at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases.

When talking about **tribological** improvement of moving parts, new aspect of the nanocoatings comes with new compositions like nanocomposites structures consisting of crystalline carbides, diamond-like carbon (DLC) and metal dichanogenides[4] for wear-resistant and low friction applications; TiB_xN_y or TiB_xC_y[5] based coatings ,with excellent tribological and mechanical properties (hardness up to 50-70 GPa and elastic modulus around 500GPa) and nanocomposite coatings formed by hard nanocrystalline phases within a metal matrix, such as TiN in Ti[6], Zr-Y-N[7] for wear resistant applications. The most common and versatile deposition method for this kind of layer is PVD. For example, CrAlN is a multiphase coating composed of CrN nanocrystalline grains where Al is in solid solution within the grains or in the boundary region as an amorphous mixture of Al-N and Al-O.

	nc-CrAlN	CrN standard
Hardness	35 GPa	20 GPa
Grain size	<12 nm	-
Adherence	60 N	45 N
Temperature resistance	>850 ºC	700 ºC

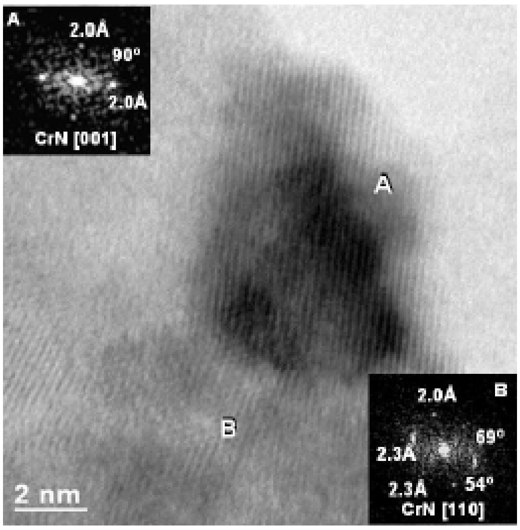


Fig 1. CrNAl sputtered nanocoating.TEM.(Fundacion INASMET)

Thermal and mechanical protection nanostructured layers deposited via thermal spraying are also being developed. The relation between grain growth and the thermal diffusivity of yttria stabilized zirconia nanostructured thermal barrier coatings could be optimized to increase the component durability and the reliability of the parts. High temperatures of operation are reported for these nanocoatings with various porosities[8][9]. Excellent mechanical properties and high coefficient of thermal expansion together with the low thermal conductivities have been reported.

[4] A.A. Voevodin, J.S. Zabinski; Thin Solid Films 370 (2000) 223-231
[5] P.H. Mayrhofer, C. Mitterer; Surf. Coat. Technol. 133/134 (2000) 131
[6] M. Misina, J. Musil, S. Kadlec, Surf. Coat. Technol. 110 (1998) 168
[7] J. Musil, H. Polakova, Surf. Coat, Technol. 127 (2000) 99
[8] Shaw et al, The dependency of microstructure and properties of nanostructured coatings on plasma spray conditions, Surf. Coating Technol, 2000, 130-180
[9] C. Zhou et al, J. Eur Ceram.Soc, 2003, 23, 1449

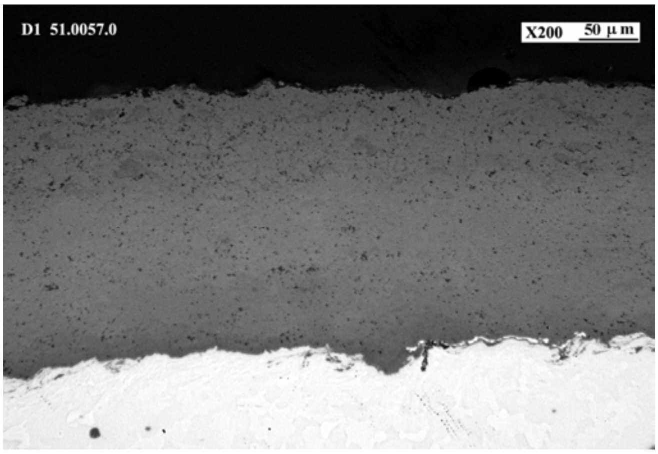


Fig 2. Yttria stabilized zirconia thermal sprayed nanocoating. SEM (Fundacion INASMET)

Nanostructured SiO_2, ZrO_2-SiO_2, Al_2O_3-SiO_2 ceramic layers obtained both by sol-gel and electrophoretic deposition are being investigated as an alternative for **corrosion protection** on aluminum alloys. Other functionalities as **abrasion resistance** are also being investigated. Also nanocomposite layers composed of conductive polymers and corrosion inhibitors (CeO_2, ZrO_2, montmorillonite) are being deposited by chemical and electrochemical techniques for corrosion protection.

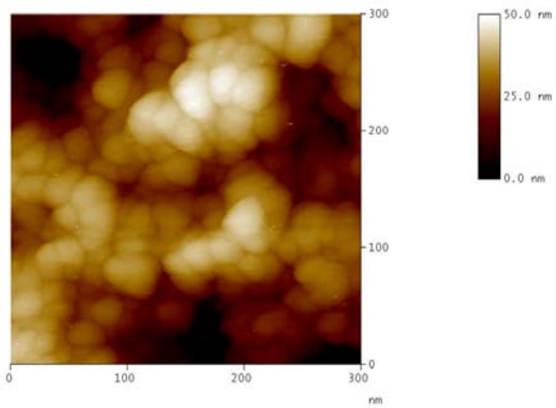


Fig.3 Nanostructured sol-gel SiO_2 layer deposited on metallic substrate. AFM (Fundacion INASMET)

Other applications that can be considered with nanocoatings are the introduction of new functionalities like anti-scratch, anti-stain, self-repairing or self-healing and specially the ability to introduce several of them in the same nanocoating without loosing most of the mechanical or tribological properties.

3. NANOCOMPOSITES

Lightweight, high strength, thermally stable materials are desirable in airframe, and engines. Lighter materials without compromises to the stiffness and crash resistance means less material and indirectly less fuel consumption and therefore less emissions.

Nanocomposites based on various metal, ceramic or plastic matrix material strengthened by metal or ceramic nanoparticles or nanoplatelets can improve the strength by 100%. But also layered silicate nanocomposites are finding applications in engine components and fuel storage tanks due to their increased lifetime, enhanced strength and elastic modulus and improved polymer barrier properties.

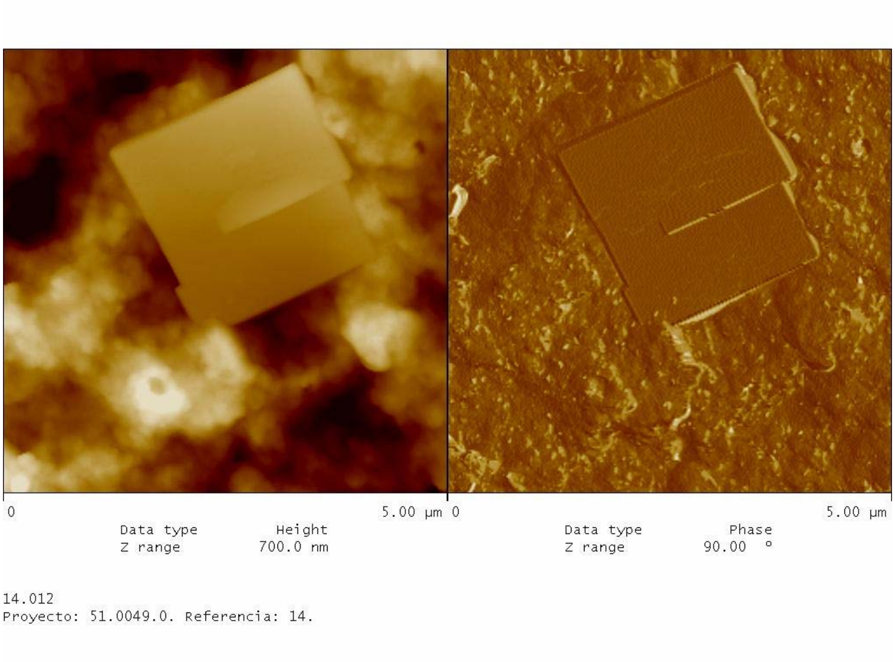


Fig 3. Nanoclay in Thermoplastic. AFM (Fundacion Inasmet)

Polymer-silicate nanocomposites have been an attractive means of improving matrix resins in carbon-fiber-reinforced composites. Organic modification of the silicate aids dispersion into the polymer matrix and provides a strong interaction between the nanoclay and the matrix. The dispersion of the layered silicate clay improves the stability as well as the stiffness, strength and barrier properties of polymers without altering current processing techniques.

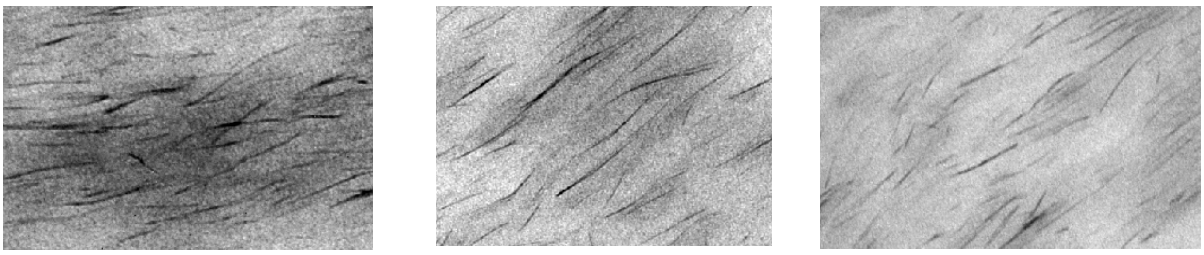
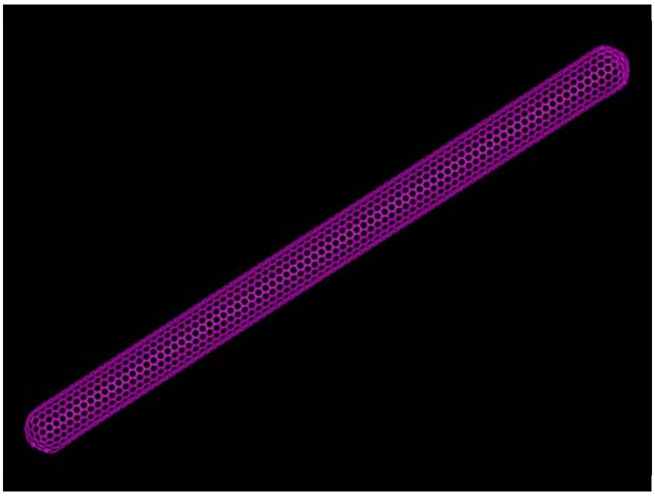


Fig 4. Nanoclay in thermoplastic at three stages a) Agglomerated b)Intercalated c) Exfoliated. TEM (Fundacion INASMET)

However carbon nanotubes or nanofibers are making a revolution in this sense, promising tensile strengths of approx 150Gpa, about 50 times that of steel with 1/5th of the weight. Breakthroughs in nanotube science, production and functionalization are leading to the development of advanced nanocomposites for aerospace applications. Carbon nanotubes possess many unique characteristics that promise to revolutionize the world of structural materials resulting in significant impact on our capability to build lighter, smaller and higher performance structures. There are publications showing the excellent properties of nanocomposites reinforced both with single wall and multi wall carbon nanotubes designed to provide the following features: ultra-lightweight, chemical stability, high thermal and electrical conductivity, low permeability, hydrolytic oxidation resistance, radiation resistance, atomic oxygen resistance, low solar absorption, high emissivity, low coefficient of thermal expansion and mechanical durability. One of the main issues dealing with the carbon nanotubes is the difficulties in introducing them in matrixes of different materials arising on one side due to the high stability of carbon nanotubes and on the other side due to the tendency to get agglomerated or tangled together.



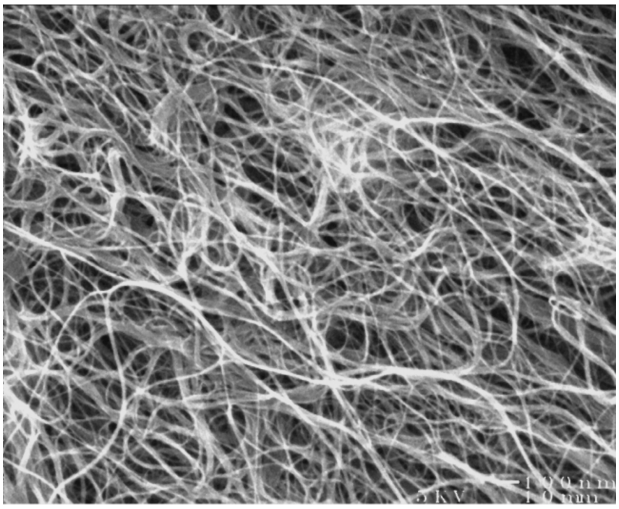


Fig 6. a) Ideal Carbon Nanotube b) Tangled carbon nanotubes

Polymers such as epoxy, thermoplastics, gels, as well as PMMA have been used as the matrix, however most of the developments have been limited by the problems with the dispersion of the fillers as well as the load transfer across the CNT polymer interface.

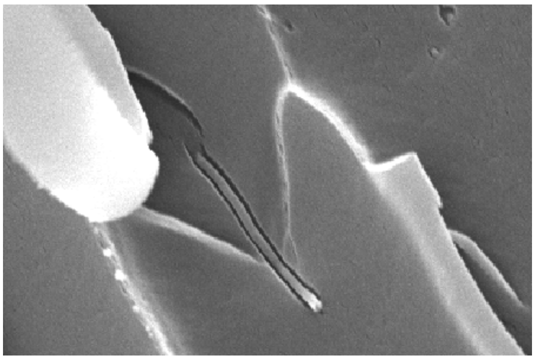


Fig 7. Nanotube in epoxi. SEM (Fundacion INASMET)

Other applications that can be considered with nanotube reinforced composites are:

- Reliability and control via the piezoelectricity of the CNT
- Lightning protection
- Heat or fire protection: flame-retardant or thermal conductivity control

4. NANOPOROUS MATERIALS or NANOPARTICLES for others like: air filtering, components of energy production and storage, sensors

There are other nanomaterials that have a great potential in aerospace components such as:

- New nanoporous filters and sensors for comfort and safety, control of air quality and safety
- Noise reduction via controlled size nanopores
- New catalysts: heterogeneous catalysts use 1-50nm nanoparticles. Zeolites and new artificial high-surface area materials may be interesting new catalysts
- Sensors based on nanoparticles able to obtain new selectivities and increased sensibility

5. OTHER CHALLENGES

Technical challenges already explained like the handling of nanomaterials should be taken into consideration when trying to establish the **time to market** of all these products. A lot of developments and funding are addressing these issues.

Cost of the nanomaterials especially CNT is an issue which is evolving daily and is considered to have an end in the near future as soon as companies like NEC start producing in mass this kind of products. Suppliers may be limited in CNT as far as the **patent** portfolios of some big Japanese companies does not become obsolete.

Lack of specifications related to the metrology of this nanoproducts is a challenge which will take longer, as some of the **measurements** that are being implemented to obtain the specifications are very much dependent on the test itself or on the materials and difficult to be standardized.

Toxicity issues are specially relevant when talking about industrialization of the nanoproducts and a lot of research is being considered all over the world. European Comission as well as NNI in the United States is funding in depth investigation on the toxicity of nanomaterials especially nanotubes.

Future developments and research investment is going to continue to be critical in order to obtain more reproducible products in the market. The re-focussing of the research coming from industries could accelerate the time to market of this product, by not leaving scientists work on marginal problems and concentrating on the important issues. Disruptive technologies are always long to implement.

6. CONCLUSIONS

The great potential of nanomaterials in the Aerospace industry has been revised as well as the major challenges to be overcome to bring real products into the market. Some of the concerns for the aerospcae and defense are related to noise, reliability, safety or weight of the structures. Revolutionary solutions can be found within advanced nanomaterials like nanoporous membranes, self-healing nanomaterials, high strength nanocomposites or adaptive and actuating nanostructures.

Technical challenges dealing with the knowledge, handling and characterization of these nanomaterials should be well addressed by the research community but with the assessment of industries dealing with the daily problems and challenges.

Other fundamental aspects should be taken into consideration to integrate nanomaterials in the Aerospace industries, like cost, standardization, or toxicity.